

## SUPPORTING INFORMATION

### FeCl<sub>3</sub>/Diorganyl Dichalcogenides Promoted Cyclization of 2-organochalcogen-3-alkynylthiophenes: Synthesis of Chalcogenophene[2,3-*b*]thiophenes

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#### Materials and Methods

Proton nuclear magnetic resonance spectra (<sup>1</sup>H NMR) were obtained at 200 MHz on a Bruker DPX-200 NMR spectrometer or at 400 MHz on a Bruker DPX-400 NMR spectrometer. Spectra were recorded in CDCl<sub>3</sub> solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of CDCl<sub>3</sub> or tetramethylsilane (TMS) as the external reference. Data are reported as follows: chemical shift ( $\delta$ ), multiplicity, coupling constant ( $J$ ) in Hertz and integrated intensity. Carbon-13 nuclear magnetic resonance spectra (<sup>13</sup>C NMR) were obtained either at 50 MHz on a Bruker DPX-200 NMR spectrometer or at 100 MHz on a Bruker DPX-400 NMR spectrometer. Spectra were recorded in CDCl<sub>3</sub> solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of CDCl<sub>3</sub>. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sex (sextet), dd (double doublet), and m (multiplet). High resolution mass spectra were recorded on a Kratos MS50TC double focusing magnetic sector mass spectrometer using EI at 70 eV. Column chromatography was performed using Merck Silica Gel (230-400 mesh) following the methods described by Still.<sup>1</sup> Thin layer chromatography (TLC) was performed using Merck Silica Gel GF<sub>254</sub>, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine vapor, or acidic vanillin. Most reactions were monitored by TLC for disappearance of starting material. The following solvents were dried and purified by distillation from the reagents indicated: tetrahydrofuran from sodium with a benzophenone ketyl indicator. All other

(<sup>1</sup>) Still, W.C., Kahn, M., Mitra, A.; *J. Org. Chem.* **1978**, *43*, 2923.

solvents were ACS or HPLC grade unless otherwise noted. Air- and moisture-sensitive reactions were conducted in flame-dried or oven dried glassware equipped with tightly fitted rubber septa and under a positive atmosphere of dry nitrogen or argon. Reagents and solvents were handled using standard syringe techniques. Temperatures above room temperature were maintained by use of a mineral oil bath with an electrically heated coil connected to a Variac controller.

### **General Procedure for the Preparation of the 2-alkylchalcogen-3-alkynylthiophenes 1.**

To a two-necked round-bottomed flask under an argon atmosphere *n*-butyllithium (20 mmol, 1.5 M in hexane, 13.5 mL) was added dropwise to a solution of appropriate 3-alkynylthiophene (20 mmol) in freshly distilled dry THF (100 mL) at -78°C. The reaction mixture was then stirred for 30 minutes at this temperature and was allowed to warm to -40°C and elemental chalcogen (20 mmol) was added in one portion and the reaction was then stirred for an additional 1 h at this temperature. Appropriate alkylbromide (25 mmol) was added at -10°C and the reaction mixture was stirred for 2 h at room temperature, quenched with saturated NH<sub>4</sub>Cl (50 mL) and extracted with ethyl acetate (3×50 mL). The combined organic layers were dried over MgSO<sub>4</sub> and concentrated under vacuum. The purification was carried out by flash chromatography on silica gel using hexane as the eluent.

**General Procedure for Iron-Promoted cyclization of 2-butylchalcogen-3-alkynylthiophenes and Diorganoyl Dichalcogenides.** To a Schelenck tube, under air atmosphere, containing a mixture of FeCl<sub>3</sub> (0.25 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added the appropriate diorganoyl dichalcogenide (0.55 equiv). The resulting solution was stirred for 5 min at room temperature. After this 2-butylchalcogen-3-alkynylthiophenes (0.25 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was added and resulting solution was stirred under room temperature for 1 hour. After this the solution was diluted with dichloromethane (10 mL), and washed with saturated aq NH<sub>4</sub>Cl (3 × 10 mL). The organic phase was separated, dried over MgSO<sub>4</sub>, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using hexane as the eluent.

**5-phenyl-4-(phenylseleno)selenophene[2,3-*b*]thiophene (2a).** Yield: 0.087 g, 83%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): δ 7.56-7.49 (m, 2H), 7.41-4.31 (m, 4H), 7.24-7.12 (m, 6H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz):  $\delta$  153.9, 151.9, 136.0, 133.8, 132.5, 129.8, 129.5, 129.2, 128.4, 128.3, 128.2, 126.1, 123.4, 113.6. MS (relative intensity) *m/z*: 419 (99), 339 (91), 260 (75), 218 (43), 171 (100), 139 (61), 77 (21). HRMS calcd for C<sub>18</sub>H<sub>12</sub>SSe<sub>2</sub>: 419.8990. Found: 719.9005.

**5-phenyl-4-(4-tolylphenylseleno)selenophene[2,3-*b*]thiophene (2b).** Yield: 0.081 g, 75%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.54-7.51 (m, 2H), 7.36-7.27 (m, 4H), 7.14-7.10 (m, 3H), 6.93 (d, *J* = 7.89 Hz, 2H), 2.22 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz):  $\delta$  153.3, 152.0, 136.0, 135.9, 133.7, 129.9, 129.8, 129.7, 128.5, 128.3, 128.2, 128.1, 123.4, 114.0, 20.9. MS (relative intensity) *m/z*: 432 (74), 354 (95), 274 (53), 218 (41), 171 (100), 139 (63), 91 (37), 65 (10). Anal. calcd for C<sub>19</sub>H<sub>14</sub>SSe<sub>2</sub>: C, 52.79; H, 3.26. Found: C, 52.90; H, 3.31.

**5-phenyl-4-(4-fluorophenylseleno)selenophene[2,3-*b*]thiophene (2c).** Yield: 0.074 g, 68%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.54-7.49 (m, 2H), 7.39-7.33 (m, 4H), 7.24-7.11 (m, 3H), 6.89-6.81 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  161.9 (d, *J* = 246.63 Hz), 153.6, 151.8, 136.1, 133.9, 132.1, (d, *J* = 8.1 Hz) 132.6, 129.9, 128.5, 128.3, 126.7 (d, *J* = 3.66 Hz), 123.3, 116.3 (d, *J* = 21.9), 114.3. MS (relative intensity) *m/z*: 436 (77), 358 (80), 263 (54), 218 (48), 171 (100), 139 (66), 89 (15). HRMS calcd for C<sub>18</sub>H<sub>11</sub>FSSe<sub>2</sub>: 437.8896. Found: 437.8905.

**5-phenyl-4-(4-chlorophenylseleno)selenophene[2,3-*b*]thiophene (2d).** Yield: 0.085 g, 75%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.52-7.49 (m, 2H), 7.41-7.33 (m, 4H), 7.11 (s, 5H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz):  $\delta$  154.3, 151.6, 135.9, 132.2, 131.5, 130.8, 130.7, 129.8, 129.3, 128.6, 128.4, 128.3, 123.2, 113.3. MS (relative intensity) *m/z*: 453 (26), 374 (79), 338 (60), 263 (56), 219 (47), 171 (100), 139 (59). HRMS calcd for C<sub>18</sub>H<sub>11</sub>ClSSe<sub>2</sub>: 453.8600. Found: 453.8623.

**5-phenyl-4-(phenyltelluro)selenophene[2,3-*b*]thiophene (2e).** Yield: 0.090 g, 77%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  7.48-7.03 (m, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  156.2, 155.0, 137.7, 135.8, 134.7, 130.1, 129.3, 128.4, 128.2, 127.4, 127.2, 124.9, 115.8, 99.9. MS (relative intensity) *m/z*: 467 (65), 339 (87), 259 (81), 218 (42), 170 (100), 138 (72), 77 (76). HRMS calcd for C<sub>18</sub>H<sub>12</sub>SSeTe: 469.8887. Found: 469.8909.

**4-(butylseleno)-5-phenylselenophene[2,3-*b*]thiophene (2f).** Yield: 0.065 g, 65%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  7.61-7.35 (m, 7H), 2.66 (t, *J* = 7.3 Hz, 2H), 1.44 (quint, *J* = 7.3 Hz, 2H), 1.20 (sext, *J* = 7.3 Hz), m0.74 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  152.8, 151.6, 136.6, 133.2, 129.9, 128.2, 128.1, 127.9, 123.4, 114.7, 32.2, 28.6,

22.5, 13.3. MS (relative intensity)  $m/z$ : 399 (44), 341 (57), 263 (100), 183 (64), 170 (32), 138 (59), 57 (11). HRMS calcd for  $C_{16}H_{16}SSe_2$ : 399.9303. Found: 399.9317.

**4-(butyltelluro)-5-(phenylseleno)selenophene[2,3-*b*]thiophene (2g).** Yield: 0.060 g, 54%.  $^1H$  NMR ( $CDCl_3$ , 200 MHz):  $\delta$  7.55-7.37 (m, 7H), 2.66 (t,  $J$  = 7.3 Hz, 2H), 1.54 (quint,  $J$  = 7.3 Hz, 2H), 1.19 (sext,  $J$  = 7.3 Hz), 0.76 (t,  $J$  = 7.3 Hz, 3H).  $^{13}C$  NMR ( $CDCl_3$ , 50 MHz):  $\delta$  155.5, 154.2, 137.8, 133.9, 130.2, 128.2, 128.1, 127.3, 124.9, 97.1, 33.5, 24.7, 13.3, 9.1. MS (relative intensity)  $m/z$ : 447 (7), 281(18), 264 (68), 207 (48), 184 (100), 139 (55), 73 (40). HRMS calcd for  $C_{16}H_{16}ClSSeTe$ : 449,9200. Found: 449.9213.

**4-(phenylseleno)-5-(4-tolyl)selenophene[2,3-*b*]thiophene (2h).** Yield: 0.082 g, 76%.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  7.42 (d,  $J$  = 8.2 Hz, 2H), 7.30 (d,  $j$  = 5.3 Hz, 1H), 7.23-7.09 (m, 8H), 2.36 (s, 3H).  $^{13}C$  NMR ( $CDCl_3$ , 100 MHz):  $\delta$  154.2, 151.9, 138.4, 132.6, 131.4, 129.6, 129.5, 129.1, 129.0, 128.1, 126.0, 123.4, 113.3, 99.5, 21.2. MS (relative intensity)  $m/z$ : 433 (59), 353 (82), 275 (60), 261 (42), 197 (100), 151 (51), 77 (32). HRMS calcd for  $C_{19}H_{14}SSe_2$ : 433,9147. Found: 433.9163.

**5-(4-methoxyphenyl)-4-(phenylseleno)selenophene[2,3-*b*]thiophene (2i).** Yield: 0.091 g, 81%.  $^1H$  NMR ( $CDCl_3$ , 400 MHz):  $\delta$  7.46 (d,  $J$  = 8.8 Hz, 2H), 7.32-7.18 (m, 7H), 6.90 (d,  $J$  = 8.8 Hz, 2H), 3.82 (s, 3H).  $^{13}C$  NMR ( $CDCl_3$ , 50 MHz):  $\delta$  159.9, 154.1, 152.0, 133.3, 133.0, 132.7, 131.1, 129.5, 129.2, 128.6, 128.0, 126.1, 123.4, 113.8, 55.3. MS (relative intensity)  $m/z$ : 448 (83), 370 (100), 293 (65), 277 (62), 250 (36), 184 (26), 169 (45) 77(14). Anal. calcd for  $C_{19}H_{14}OSSe_2$ : C, 50.90; H, 3.15. Found: C, 51.09; H, 3.19.

**5-(4-chlorophenyl)-4-(phenylseleno)selenophene[2,3-*b*]thiophene (2j).** Yield: 0.085 g, 75%.  $^1H$  NMR ( $CDCl_3$ , 200 MHz):  $\delta$  7.48-7.43 (m, 2H), 7.36-7.32 (m, 3H), 7.22-7.12 (m, 6H).  $^{13}C$  NMR ( $CDCl_3$ , 50 MHz):  $\delta$  152.2, 152.0, 134.5, 134.4, 133.9, 132.3, 131.0, 129.5, 129.2, 128.5, 128.4, 126.3, 123.4, 114.2. MS (relative intensity)  $m/z$ : 453 (27), 374 (87), 338 (56), 262 (100), 182 (34), 169 (39), 137 (34), 77 (21). HRMS calcd for  $C_{18}H_{11}ClSSe_2$ : 453,8600. Found: 453.8608.

**5-hexyl-4-(phenylseleno)selenophene[2,3-*b*]thiophene (2k).** Yield: 0.079 g, 74%.  $^1H$  NMR ( $CDCl_3$ , 200 MHz):  $\delta$  7.63-7.10 (m, 7H), 3.11 (t,  $J$  = 7.3 Hz, 2H), 1.74-1.58 (m, 2H), 1.45-1.21 (m, 6H), 0.92-0.82 (m, 3H).  $^{13}C$  NMR ( $CDCl_3$ , 50 MHz):  $\delta$  158.6, 151.3, 132.5, 131.4, 129.2, 127.8, 127.7, 125.9, 122.7, 113.8, 33.3, 32.6, 31.5, 28.7, 22.5, 14.0. MS (relative intensity)  $m/z$ : 426 (82), 356 (58), 275(100), 197 (96), 120 (44), 77 (25) . HRMS calcd for  $C_{18}H_{20}SSe_2$ : 427,9616. Found: 427.9639.

**2-phenyl-3-(phenylseleno)benzo[*d*]selenophene[2,3-*b*]thiophene (2l).** Yield: 0.073 g, 62%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  8.78-8.72 (m, 1H), 7.82-7.76 (m, 1H), 7.52-7.06 (m, 12H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz):  $\delta$  155.3, 144.3, 143.0, 138.4, 125.9, 134.7, 133.7, 130.1, 129.4, 128.5, 128.2, 125.9, 124.2, 124.1, 122.4, 122.2, 114.0. MS (relative intensity)  $m/z$ : 467 (47), 390 (45), 312 (100), 269 (41), 232 (69), 189 (62), 154 (46), 77(29). Anal. calcd for  $\text{C}_{22}\text{H}_{14}\text{SSe}_2$ : C, 56.42; H, 3.01. Found: C, 56.60; H, 3.08.

**2-phenyl-3-(4-tolylseleno)benzo[*d*]selenophene[2,3-*b*]thiophene (2m).** Yield: 0.054 g, 45%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  8.83-8.75 (m, 1H), 7.82-7.73 (m, 1H), 7.52-7.20 (m, 7H), 7.10-7.06 (m, 2H), 6.93-6.89 (m, 2H), 2.18 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz):  $\delta$  155.1, 144.3, 143.1, 138.3, 136.0, 135.7, 134.7, 130.1, 129.8, 128.6, 128.4, 128.1, 124.1, 124.0, 122.4, 122.3, 114.3, 20.9. MS (relative intensity)  $m/z$ : 482 (50), 405 (58), 311 (100), 232 (59), 207 (66), 187 (44), 154 (38), 91 (37), 73 (24). HRMS calcd for  $\text{C}_{23}\text{H}_{16}\text{SSe}_2$ : 483.9303. Found: 483.9321.

**2-butyl-3-(phenylseleno)benzo[*d*]selenophene[2,3-*b*]thiophene (2n).** Yield: 0.060 g, 54%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  8.77-8.73 (m, 1H), 7.78-7.73 (m, 1H), 7.27-7.08 (m, 7H), 3.18 (t,  $J = 7.3$  Hz, 2H), 1.65 (quint,  $J = 7.3$  Hz, 2H), 1.39 (sext,  $J = 7.3$  Hz, 2H), 0.89 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz):  $\delta$  159.6, 144.4, 142.3, 135.8, 134.5, 133.2, 129.3, 128.5, 125.8, 123.9, 123.8, 122.4, 122.1, 114.2, 34.8, 32.8, 22.2, 13.8. MS (relative intensity)  $m/z$ : 450 (61), 407 (41), 327 (80), 247 (64), 184 (39), 171 (100), 158 (29), 77 (32). HRMS calcd for  $\text{C}_{20}\text{H}_{18}\text{SSe}_2$ : 449.9460. Found: 449.9463.

**2-(2-methoxyphenyl)-3-(phenylseleno)benzo[*d*]selenophene[2,3-*b*]thiophene (2o).** Yield: 0.099 g, 80%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  8.68-8.63 (m, 1H), 7.79-7.75 (m, 1H), 7.39-6.89 (m, 11H), 3.65 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz):  $\delta$  1569, 150.5, 144.3, 142.2, 138.9, 134.5, 133.6, 132.3, 130.2, 129.0, 128.7, 125.6, 124.7, 123.9, 123.8, 122.3, 122.2, 120.1, 116.5, 110.8, 55.2. MS (relative intensity)  $m/z$ : 498 (42), 327 (100), 298 (15), 234 (21), 202 (17), 189 (10). HRMS calcd for  $\text{C}_{23}\text{H}_{16}\text{OSSe}_2$ : 499.9252. Found: 499.9252.

**2-phenyl-3-(phenylseleno)thieno[2,3-*b*]thiophene (2p).** Yield: 0.063 g, 68%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  7.61-7.56 (m, 2H), 7.44-7.08 (m, 9H), 7.03-7.00 (d,  $J = 5.3$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 50 MHz):  $\delta$  155.6, 149.5, 135.1, 134.2, 132.2, 131.5, 129.7, 129.2, 128.5, 128.3, 127.6, 126.2, 121.1, 111.8. MS (relative intensity)  $m/z$ : 372 (36), 291 (77), 213 (26), 171 (100), 77 (15). Anal. calcd for  $\text{C}_{18}\text{H}_{22}\text{S}_2\text{Se}$ : C, 58.21; H, 3.26. Found: C, 58.36; H, 3.29.

**5-phenyl-4-(phenylseleno)tellurophene[2,3-*b*]thiophene (2q).** Yield: 0.049 g, 42%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.46-7.44 (m, 2H), 7.39-7.32 (m, 5H), 7.19-7.09 (m, 5H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  157.4, 149.4, 139.7, 133.2, 129.9, 129.6, 129.1, 128.2, 127.9, 127.1, 126.0, 119.9, 119.7, 100.0. MS (relative intensity) *m/z*: 467 (9), 340 (41), 260 (42), 182 (48), 139 (100), 77 (11). Anal. calcd for C<sub>18</sub>H<sub>22</sub>S<sub>2</sub>Se: C, 58.21; H, 3.26. Found: C, 58.36; H, 3.29.

**2-phenyl-3-(phenylseleno)benzo[*d*]thieno[2,3-*b*]thiophene (2r).** Yield: 0.067 g, 64%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  8.61-8.56 (m, 1H), 7.80-7.76 (m, 1H), 7.58-7.53 (m, 2H), 7.39-7.06 (m, 10H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz):  $\delta$  150.6, 143.6, 142.5, 137.4, 134.0, 133.2, 133.2, 130.1, 129.4, 128.5, 128.3, 125.9, 124.5, 124.3, 122.8, 122.2, 112.2. MS (relative intensity) *m/z*: 422 (55), 342 (100), 264 (61), 221 (92), 77 (12). Anal. calcd for C<sub>22</sub>H<sub>14</sub>S<sub>2</sub>Se: C, 62.70; H, 3.35. Found: C, 62.81; H, 3.39.

**General procedure for palladium-catalyzed coupling reaction of 2g with boronic acid.** The solution of 4-(butyltelluro)-5-(phenylseleno)selenophene[2,3-*b*]thiophene **2g** (0.25 mmol) in MeOH (3 mL) was added to appropriate boronic acid (1.3 equiv), Pd(PPh<sub>3</sub>)<sub>4</sub> (10 mol %) and Ag<sub>2</sub>O (2 equiv). After this Et<sub>3</sub>N (4 equiv) was added, and the reaction mixture was stirred at reflux temperature for 3 h. The organic phase was separated, dried over MgSO<sub>4</sub>, and concentrated under vacuum. The residue was purified by flash chromatography and eluted with hexane.

**4-(4-bromophenyl)-5-phenylselenophene[2,3-*b*]thiophene (3a).** Yield: 0.066 g, 63%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta$  7.38-7.11 (m, 11H), 2.36 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz):  $\delta$  149.7, 146.4, 135.9, 135.8, 131.7, 131.3, 129.4, 128.9, 128.6, 128.5, 127.6, 126.1, 122.1, 121.3. MS (relative intensity) *m/z*: 417 (100), 337 (26), 258 (95), 213 (25), 169 (30), 129 (67), 106 (8). Anal. calcd for C<sub>18</sub>H<sub>11</sub>BrSSe: C, 51.69; H, 2.65. Found: C, 51.73; H, 3.10.

**5-phenyl-4-*p*-tolylselenophene[2,3-*b*]thiophene (3b).** Yield: 0.066 g, 74%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  7.36 (d, *J* = 5.3 Hz, 1H), 7.25-7.21 (m, 8H), 7.14-7.11 (m, 3H), 2.36 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  150.5, 145.6, 136.9, 136.5, 133.9, 133.2, 131.4, 129.6, 129.5, 129.2, 128.4, 128.1, 124.5, 127.3, 122.6, 21.2. MS (relative intensity) *m/z*: 354 (47), 281 (35), 207 (100), 133 (23), 73 (64). Anal. calcd for C<sub>19</sub>H<sub>14</sub>SSe: C, 64.58; H, 3.99. Found: C, 64.71; H, 4.04.

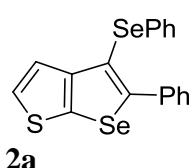
**General procedure for the reactions of intermediate 3-lithio-benzo[*b*]selenopheno[3,2-*d*]thiophene with 4-chlorobenzaldehyde.** To a two-neck

round-bottomed flask, under argon, containing a solution of 2-phenyl-3-(phenylseleno)benzo[*b*]selenopheno[3,2-*d*]thiophene (0.25 mmol) in THF (3 mL) at -78 °C was added *n*-BuLi (0.25 mmol) in one portion. The reaction mixture was stirred for 15 minutes, and then a solution of 4-chlorobenzaldehyde (0.3 mmol) in THF (1 mL) at -78 °C was added. The reaction mixture was allowed to stir at room temperature for 2 hours. After this time, the mixture was diluted with ethyl acetate (20 mL) and washed with saturated aq NH<sub>4</sub>Cl (20 mL) and water (3x20 mL). The organic phase was separated, dried over MgSO<sub>4</sub>, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using ethyl acetate/hexane (2:8) as the eluent.

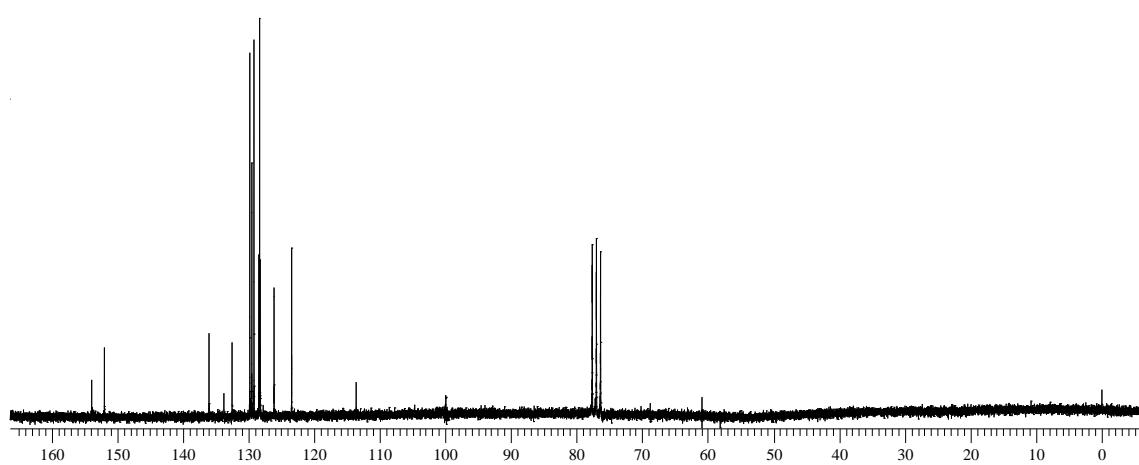
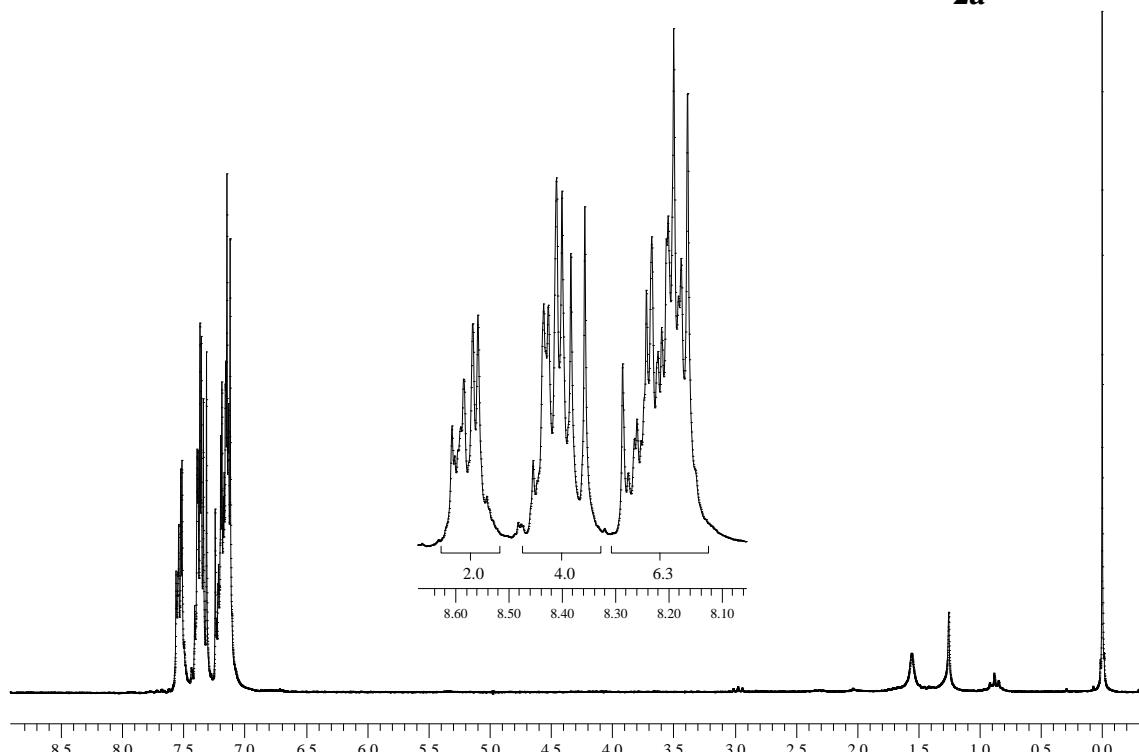
**(4-chlorophenyl)(2-phenylbenzo[*b*]selenopheno[3,2-*d*]thiophene-3-yl)methanol 4a.**

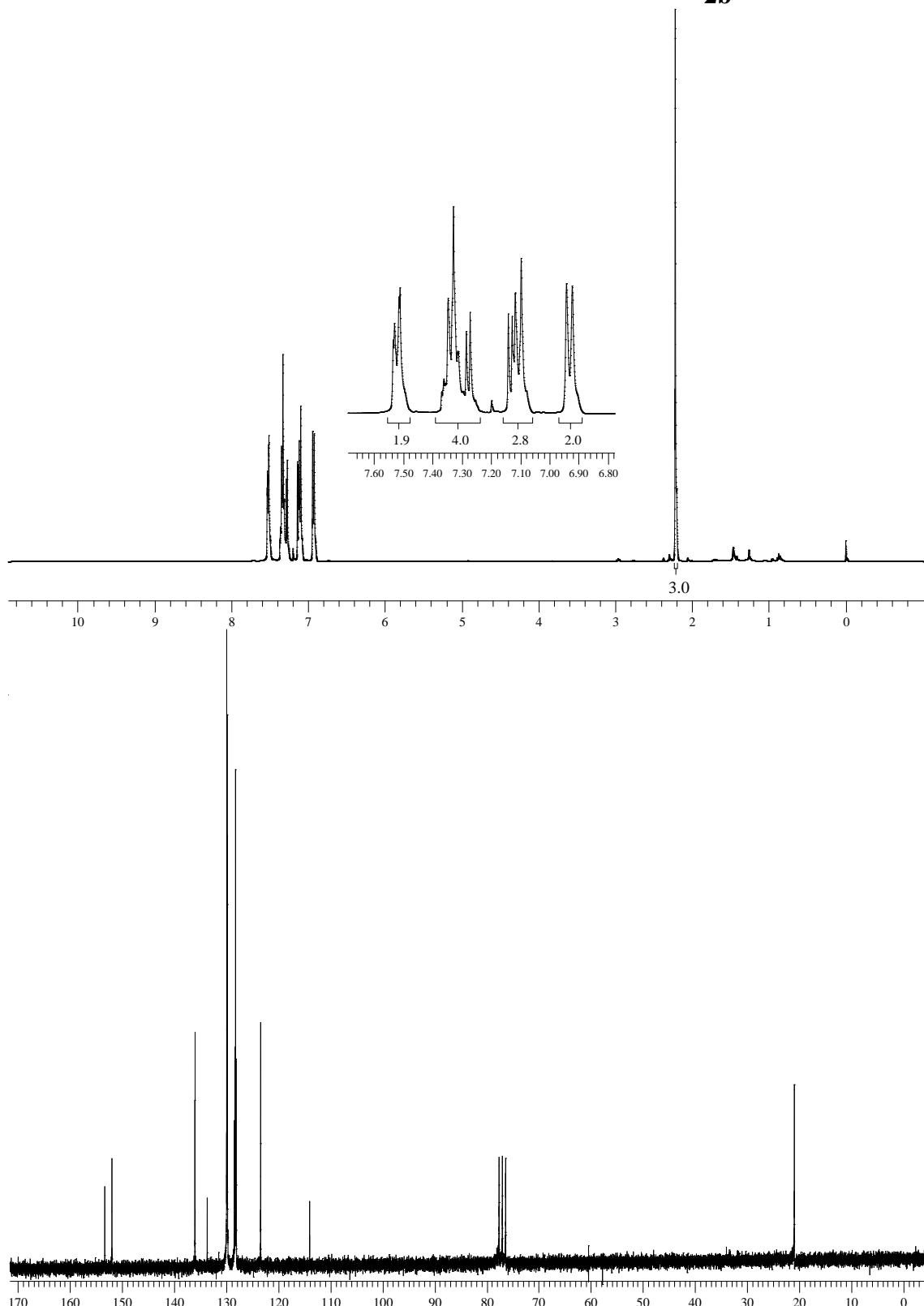
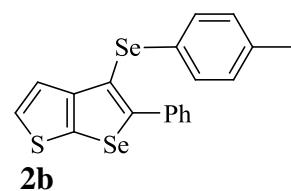
Yield: 0.067 g, 63%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): δ 7.94-7.90 (m, 1H), 7.75-7.71 (m, 1H), 7.58-7.22 (m, 11H), 6.48 (s, 1H), 2.99 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 151.8, 140.5, 139.4, 137.9, 133.8, 131.6, 128.7, 128.5, 127.6, 125.3, 124.9, 123.0, 122.8, 122.5, 115.0, 96.1, 81.8, 71.3. MS (relative intensity) *m/z*: 455 (5), 374 (29), 338 (28), 281 (37), 207 (37), 171 (72), 139 (57), 73 (41). HRMS calcd for C<sub>23</sub>H<sub>15</sub>ClOSSe: 453.9697, Found: 453.9704.

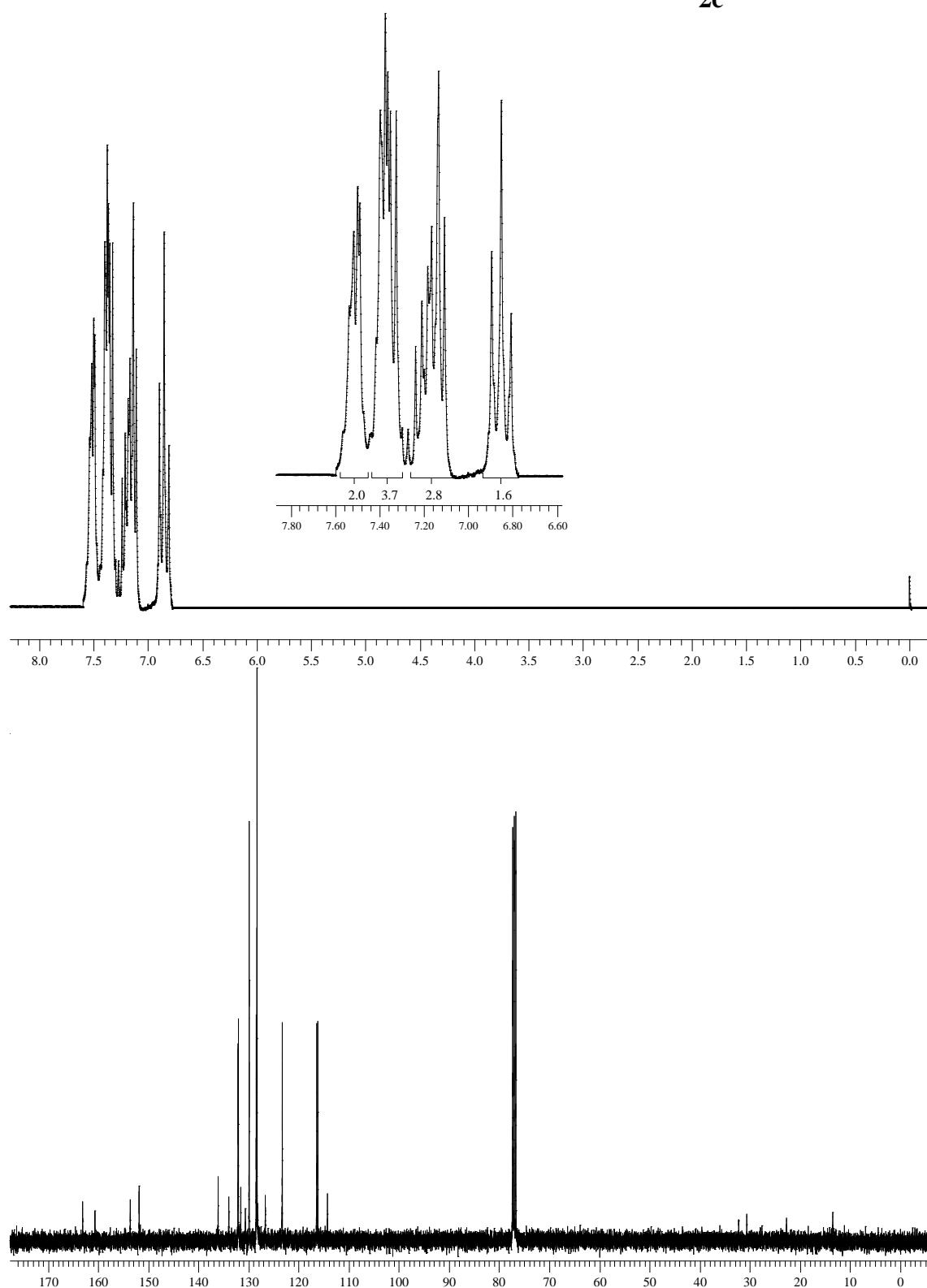
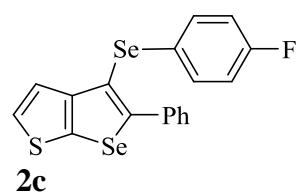
## SELECTED SPECTRA

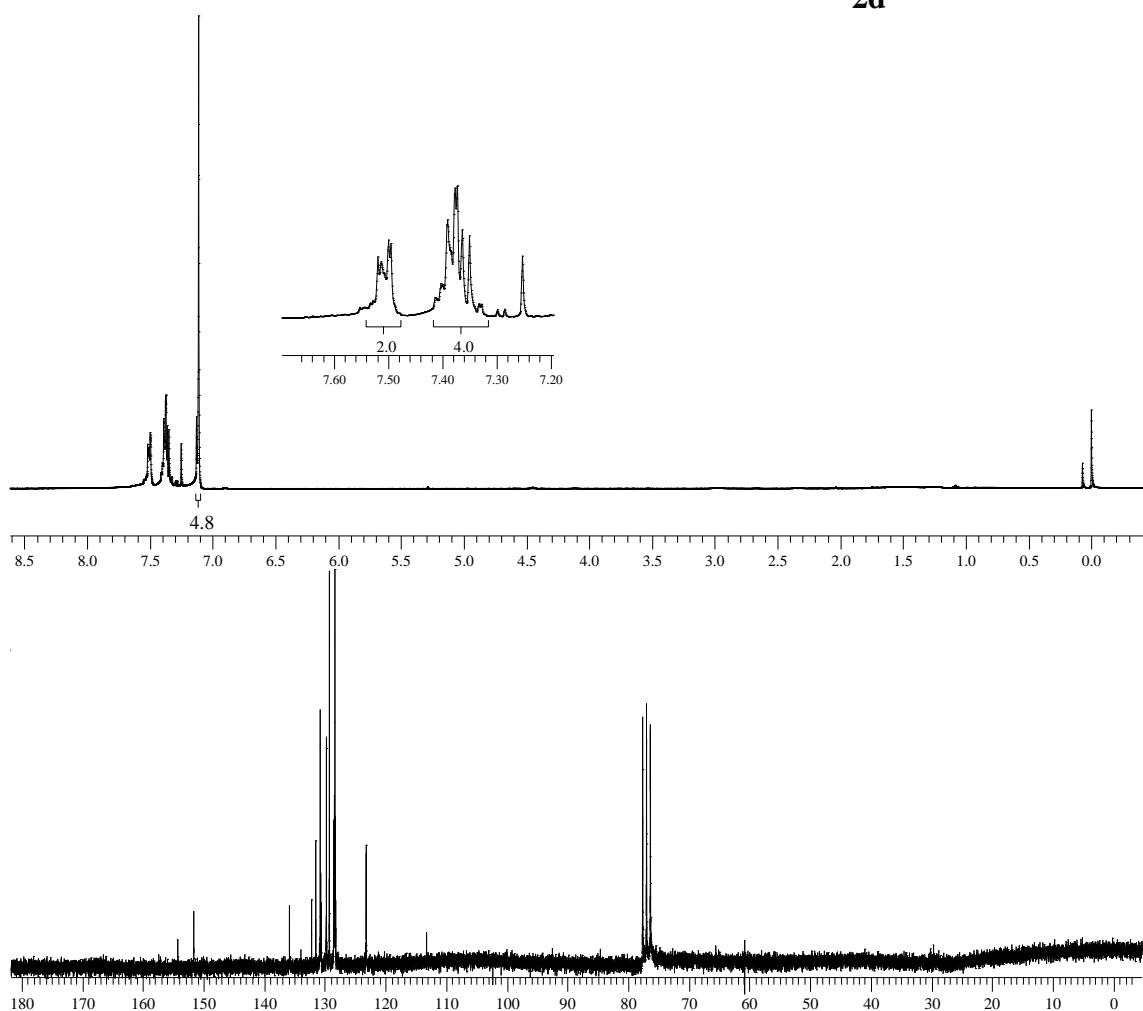
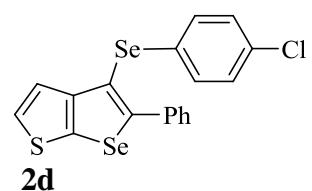


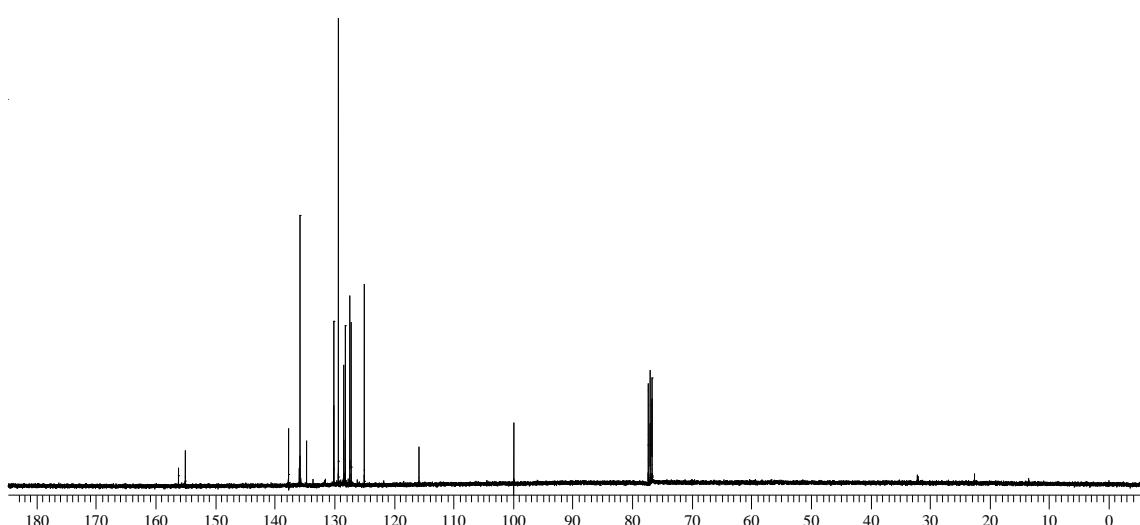
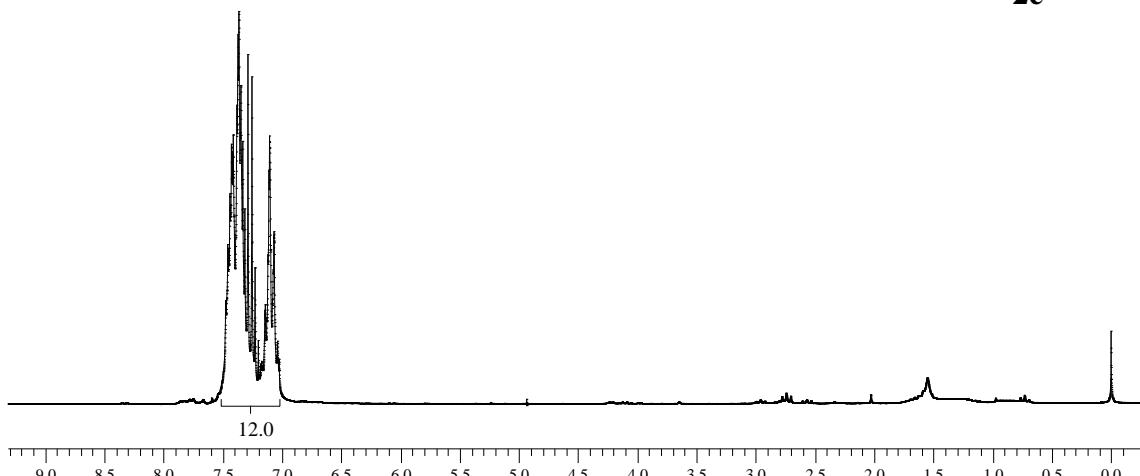
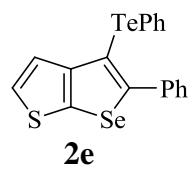
**2a**

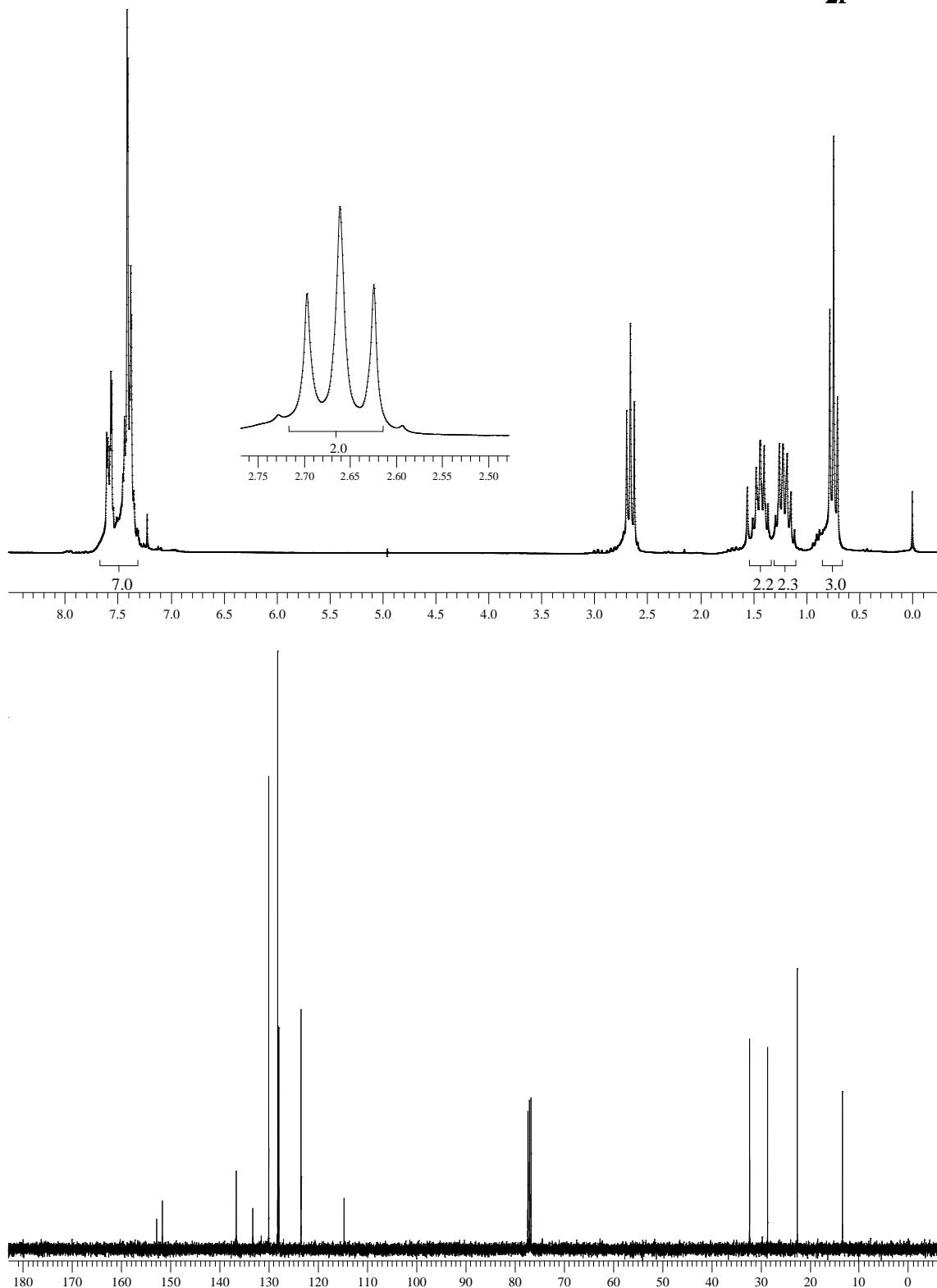
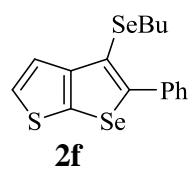


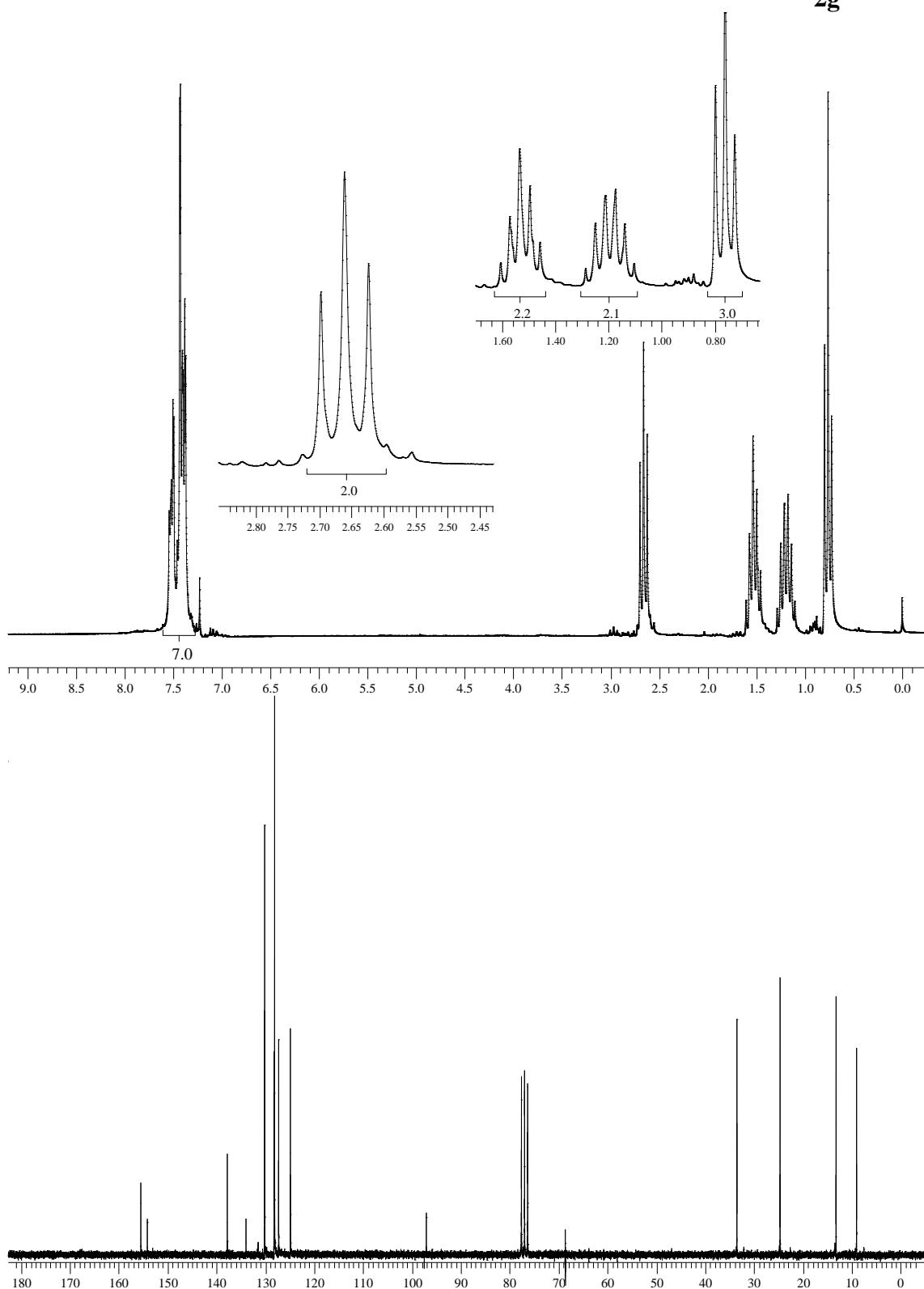
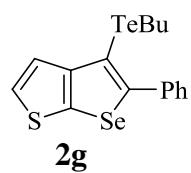


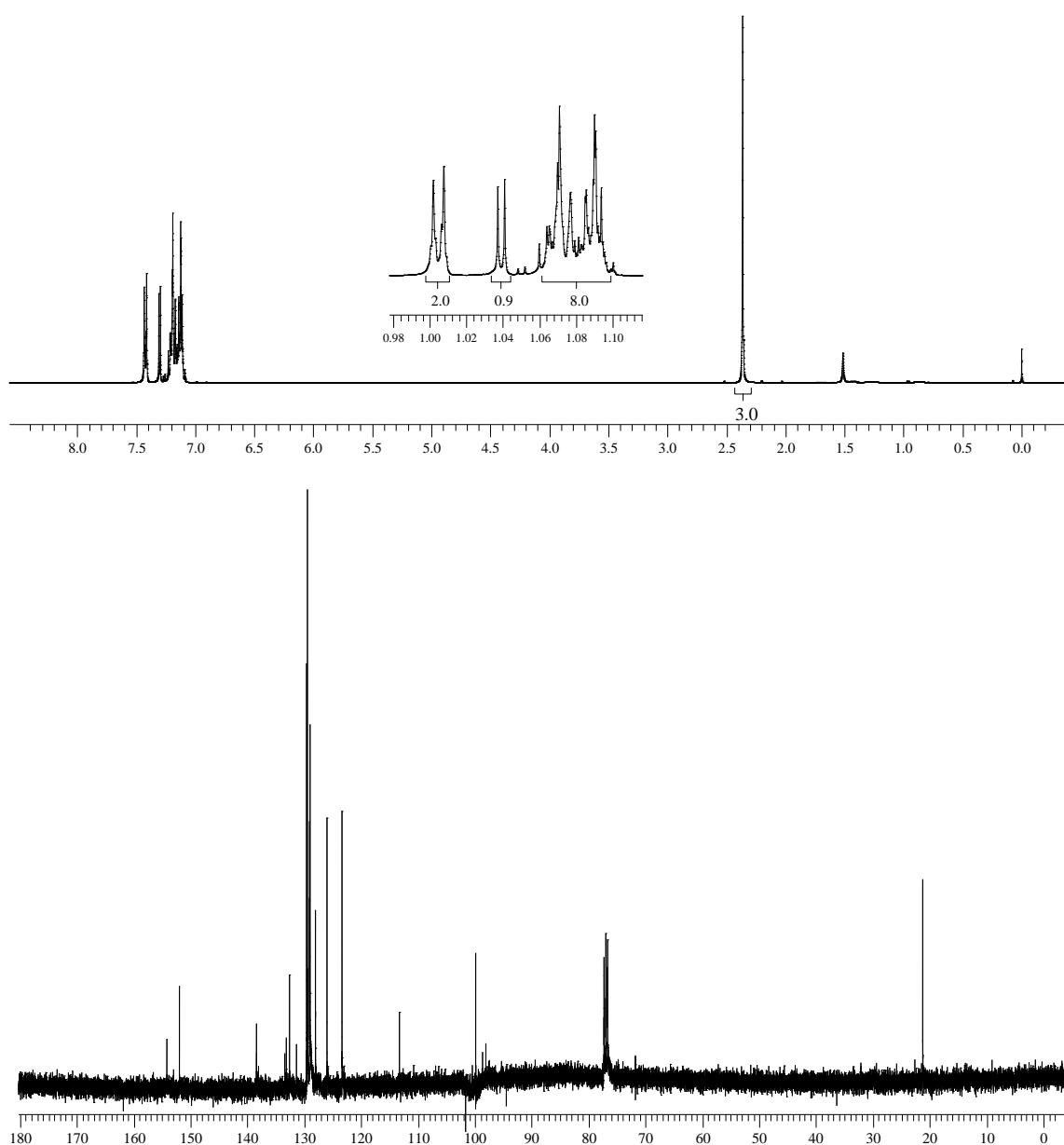
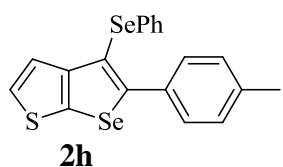


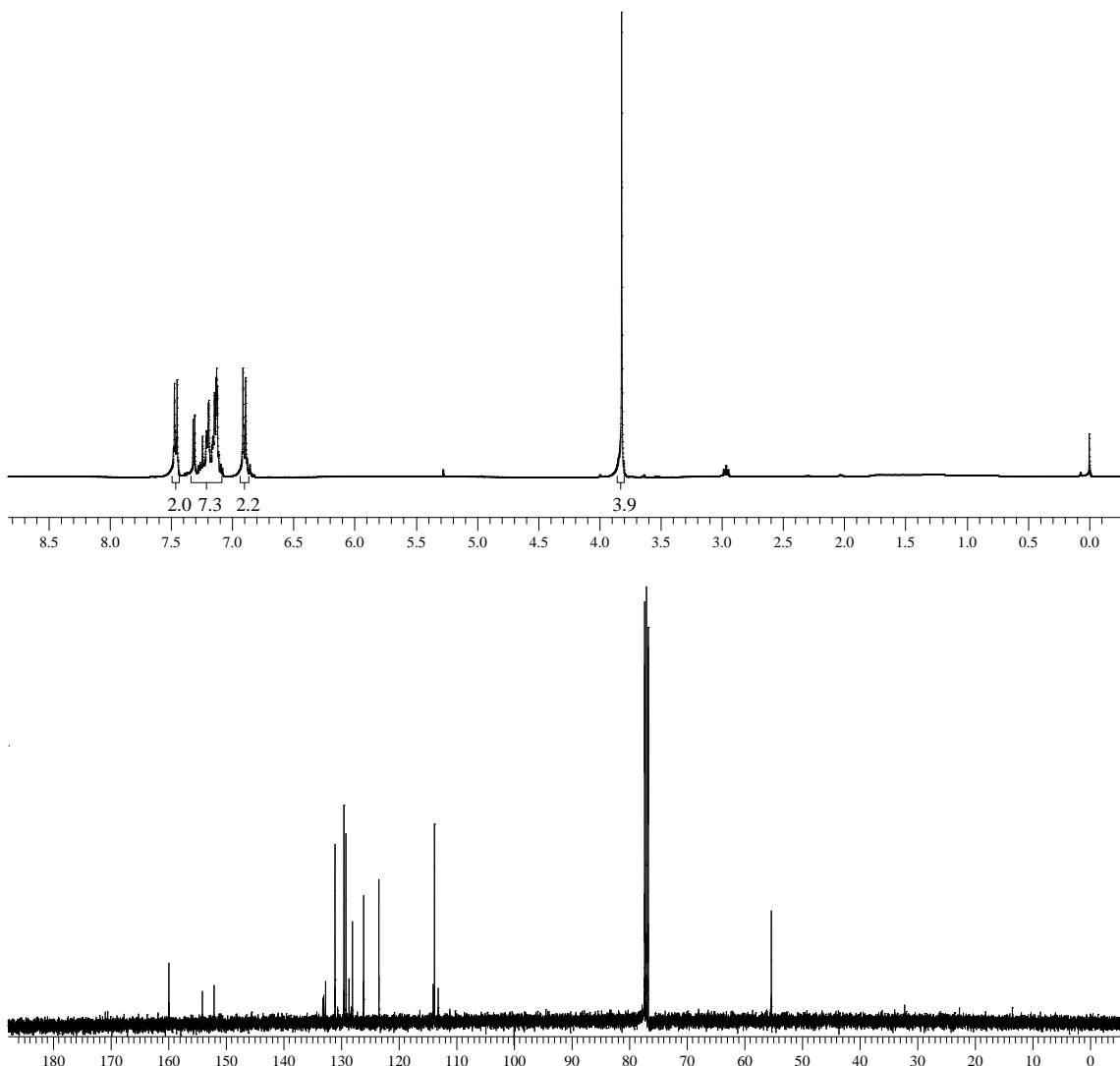
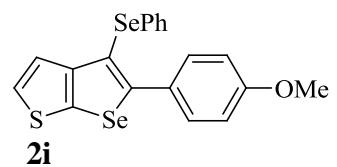


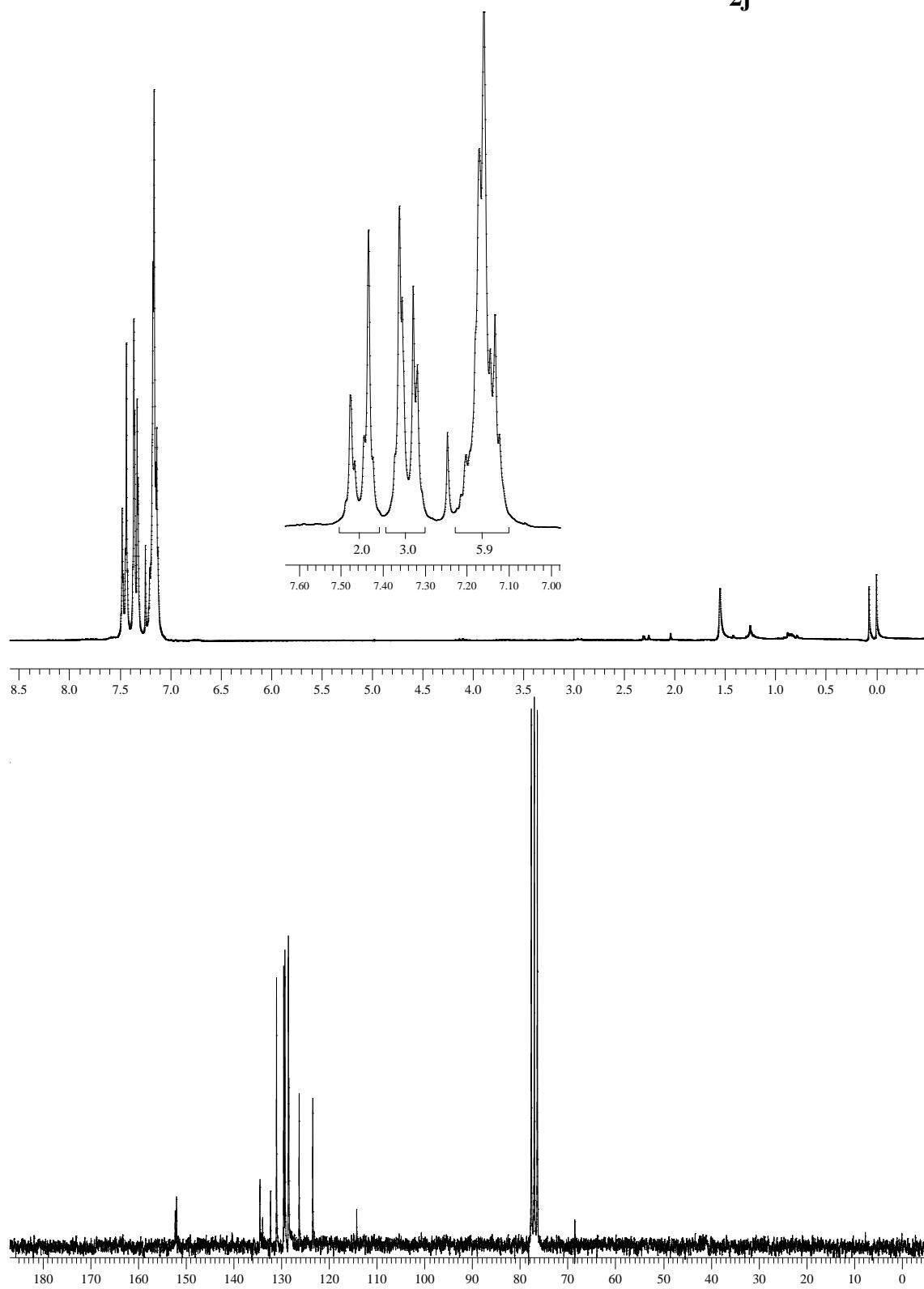
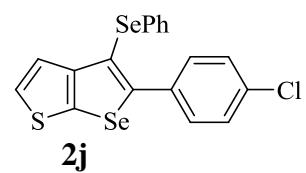


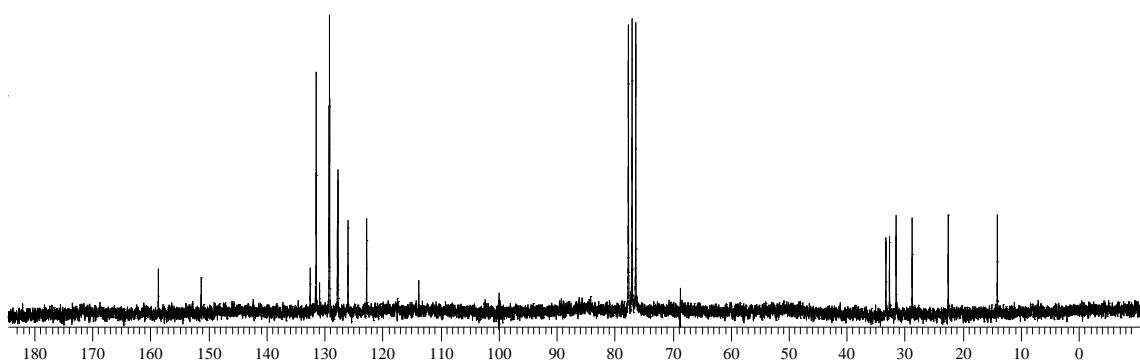
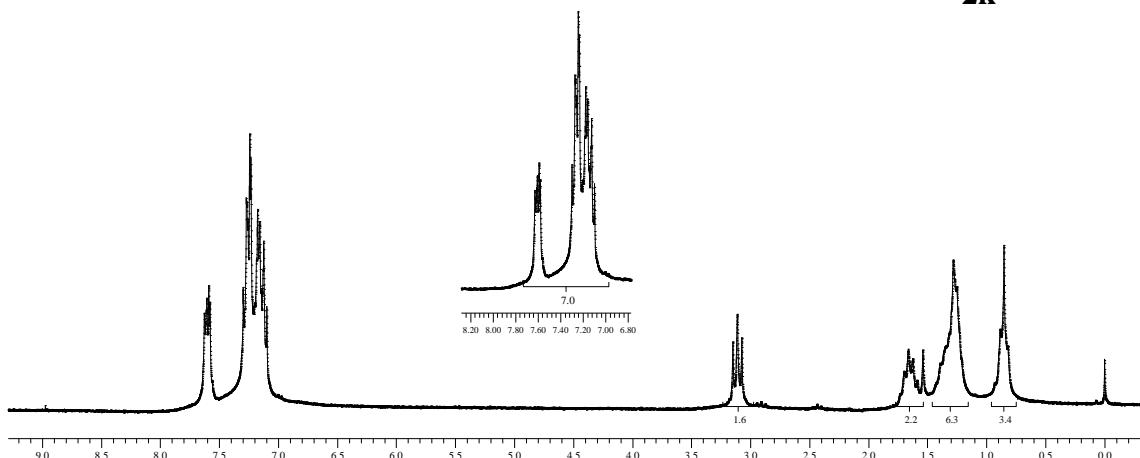
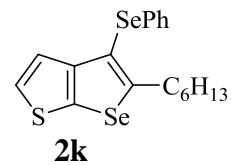


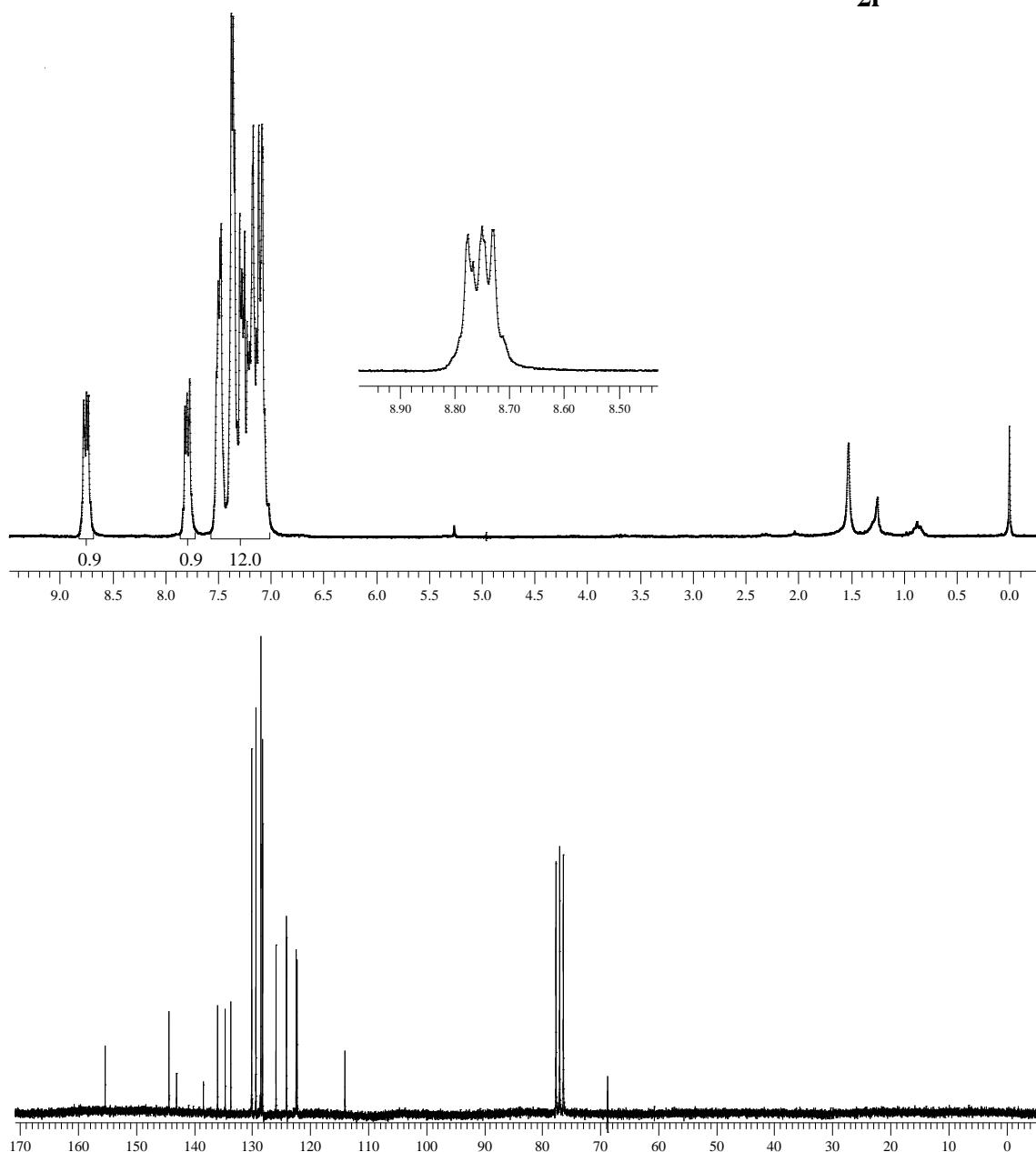
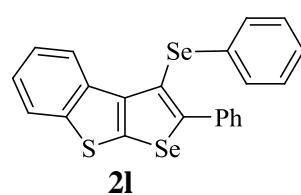


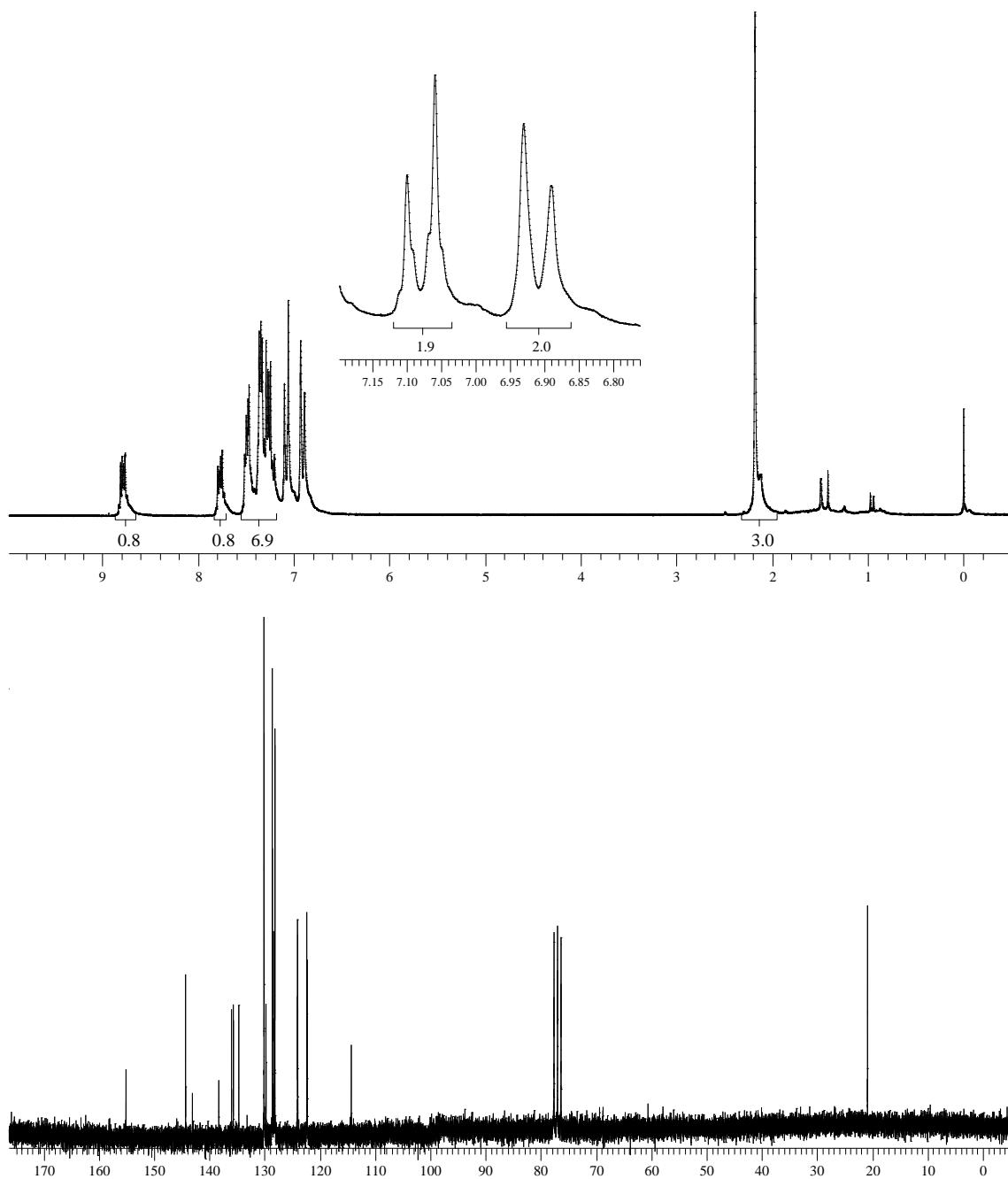
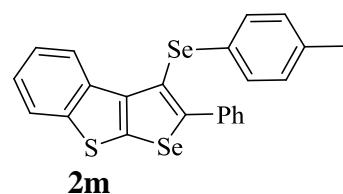


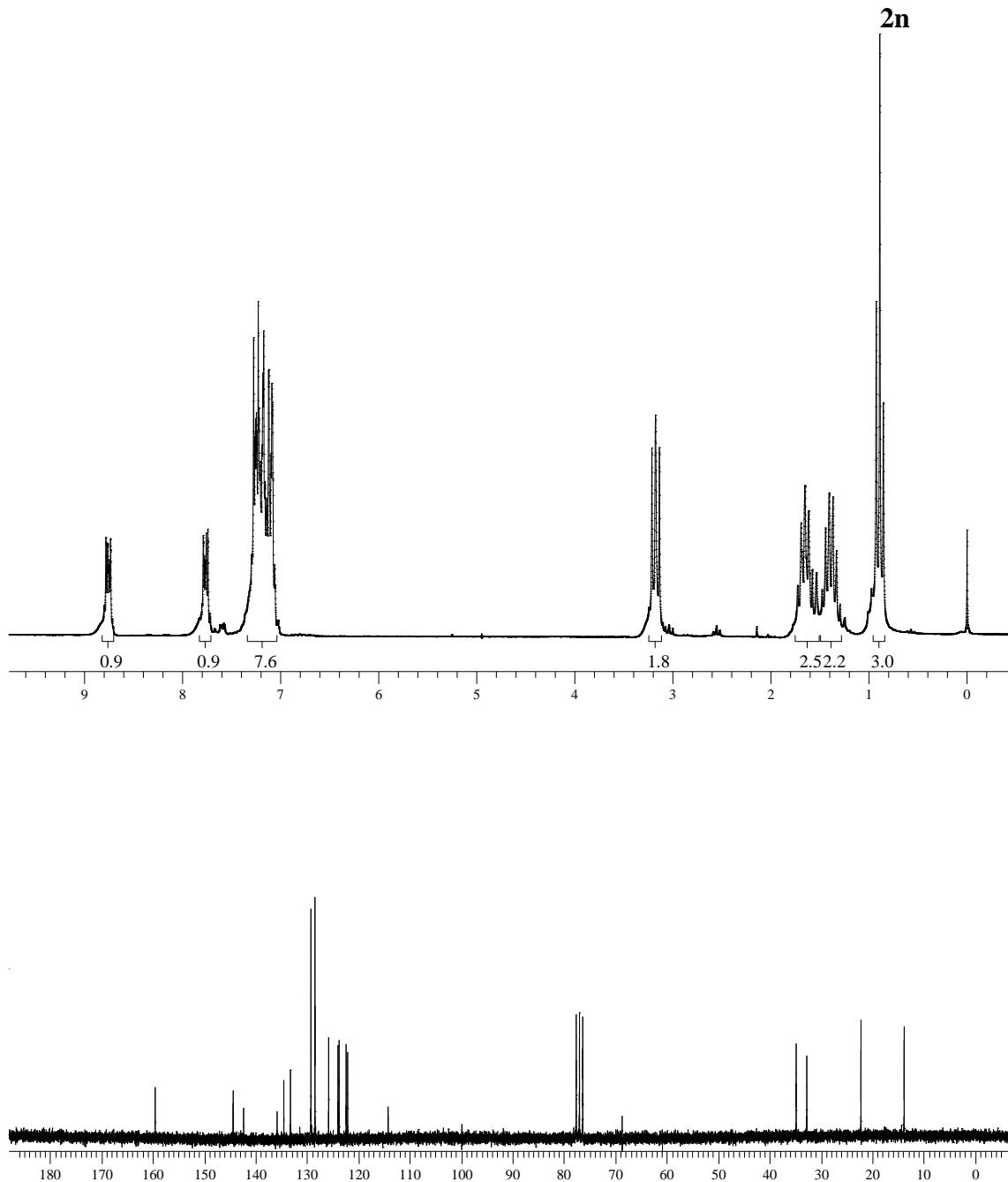
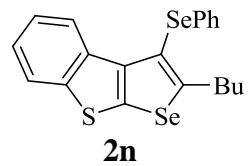


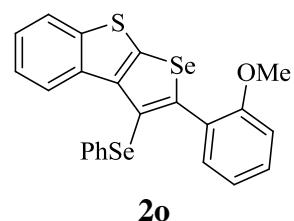












**2o**

